Pervaporation Separation of Binary Organic–Aqueous Liquid Mixtures Using Crosslinked PVA Membranes. III. Ethanol–Water Mixtures

KEW-HO LEE,[1] HAE-KYUNG KIM,[2] and JI-WON RHIM[1,2,*]

[1]Membranes and Separation Laboratory, Korea Research Institute of Chemical Technology, Daedeog-Danji, P.O. Box 9, Taejeon, South Korea 305-606; [2]Department of Chemical Engineering, Hannam University, Taejeon, South Korea 300-791

SYNOPSIS

The application of the pervaporation process in biotechnology is rapidly growing. A two stage pervaporation process could be applied to the downstream processing of ethanol fermentation. In this paper, the second stage process—a water-selective process—was investigated in detail using the crosslinked poly(vinyl alcohol) membranes with the low molecular weight of poly(acrylic acid) as the crosslinking agent. The ratio of poly(vinyl alcohol) and poly(acrylic acid) in the membrane was 90/10, 85/15, and 80/20 by weight. The prepared membranes were tested to separate the various compositions of the water–ethanol mixtures, specially 50/50 solution at 60°C and 30/70, 20/80, 10/90, and 4.4/95.6 solutions at 60, 70, and 75°C. For water : ethanol = 50 : 50 solution, the separation factor $\alpha_{w/e} = 260$ at 75°C was obtained by using a PVA/PAA = 80/20 membrane. The permeation rate and the separation factor at the azeotropic point of a water–ethanol mixture showed 30 g/m²/h and 5800 at 75°C, respectively, when a PVA/PAA = 80/20 membranes was used. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Pervaporation differs from other membrane separation processes in that the membrane constitutes a barrier between a liquid in the liquid phase and the permeate in the vapor phase. The activity of the permeating components is lowered at the permeate side by applying a vacuum or an inert gas flow. Phase change occurs because the partial pressures of the permeating components are lower than the corresponding saturation pressures. It is thus necessary to bring to the system a quantity of energy which is at least equal to the heat of evaporation.

Contaminated solvent mixtures are inevitable by-products of many processes in the mechanical, chemical, and pharmaceutical industry. Recycling or fractionation of the mixtures often is possible only after a separation of water as one of the most frequently encountered contaminants. The removal of water from such mixtures by the conventional techniques like distillation is impossible, or at least complicated, in cases where the mixture consists of high-boiling and low-boiling components (relative to water), which, additionally, form individual azeotropes with water. The membrane separation of azeotrope liquid mixtures, especially the ethanol–water mixture, because of practical interest in industry, has been studied by many investigators.[1,2] The application of pervaporation for ethanol concentration up to 70–80% from an ethanol fermentation reactor cannot yet compete with distillation; however, the last concentration step, especially at the azeotrope point, can be replaced by pervaporation instead of distillation.

Nguyen et al.[3] studied the applicability of the PVA/PAA blended films for the pervaporation separation of water–acetic acid mixtures. And also they investigated the film-forming properties for the blended PVA/PAA membranes in detail.[4,5]

In previous papers[6,7] the crosslinked poly(vinyl alcohol) (PVA) membranes with low molecular weight of poly(acrylic acid) (PAA) were characterized and also used successfully as the barrier for the phenol–water mixtures.

In principle, a two-stage pervaporation processes could be applied for the concentration of ethanol from the fermentation broth.[8] Gudernatsch et al.[9] introduced the direct application of a pervaporation unit to a fermentation reactor by using poly(dimethylsiloxane) (PDMS) hollow fiber membranes. They showed that the permeation rate was typically 0.6 kg/m^2/h and the separation factor reached up to 5.5 ($\alpha_{e/w}$), which means that the ethanol concentration of permeate could be 50 wt % because most of ethanol produced from the fermentation contains 5 to 8% ethanol. Figure 1 gives the process scheme of the coupled fermentation pervaporation unit with ethanol-selective membrane, such as poly(dimethylsiloxane), in the first stage and water-selective membrane in the second stage. During the continuous operation, the produced ethanol can be concentrated in the first downstream, so that the product inhibition effect can be deduced and the cells are returned to the fermentor. Mulder et al.[8] checked the rejection test of the D-glucose and sodium chloride for the PDMS membranes for 5 wt % ethanol in water. PDMS membranes showed complete rejection of D-glucose and sodium chloride. As a result, ethanol could be purified up to 99% or more in the second stage.

In this paper, the second separation stage is investigated in terms of the permeabilities and the separation factors in detail by using PVA/PAA blended membranes with the different crosslinking degree for the various components of the ethanol–water mixtures at 60, 70, and 75°C.

EXPERIMENTAL

Materials

Fully hydrolyzed PVA with molecular weight of 50,000 and PAA with molecular weight of 2000 (25 wt % in water) were purchased from Showa Chemical Co. and Aldrich Co., respectively. The ethanol was analytical grade from Merck. Used water was the ultrapure water produced from an MPI system.

Membrane Preparation[6]

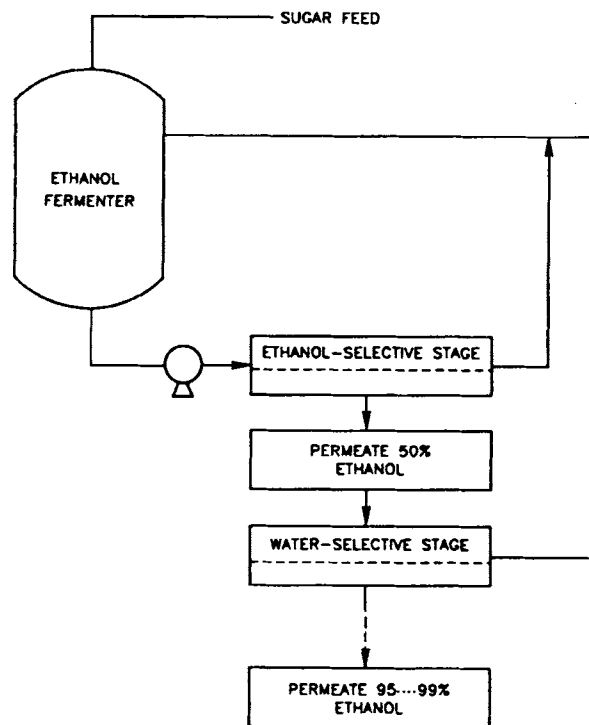Aqueous 10 wt % PVA solutions were prepared by dissolving preweighed quantities of dry PVA in ul-

Figure 1 Schematic diagram of the coupled pervaporation unit connected to the fermentor.

trapure water and heating at 90°C for at least 6 h. Aqueous 25 wt % PAA solutions were diluted to 10 wt % solutions. Then two polymer solutions were mixed together by varying each component composition to form a homogeneous solution for at least 1 day at room temperature. Homogeneous membranes were cast onto a Plexiglas plate using a Gardner knife with predetermined drawdown thickness. The membranes were allowed to dry in air at room temperature, and completely dried membranes were then peeled off. The dried blended membranes were heated in a thermosetted oven for fixed reaction time (45 min) and temperature (150°C). The resulting membranes were then stored in solutions to be separated for further use.

Pervaporation

The apparatus used in this study is illustrated in Figure 2. The pervaporation separation experiments were performed employing two stainless-steel pervaporation cell (Fig. 3). The feed mixture enters the cell through the center opening, flows rapidly through the thin channel, and leaves the cell through the side opening, which allows relatively higher fluid velocity parallel to the membrane surface. The effective membrane area is 14.2 cm^2. The 4-necked

a - Temperature controlled feed tank
b - Permeation cell
c - Vacuum manometer
d, f - Cold traps for collecting samples
e - Drying tube
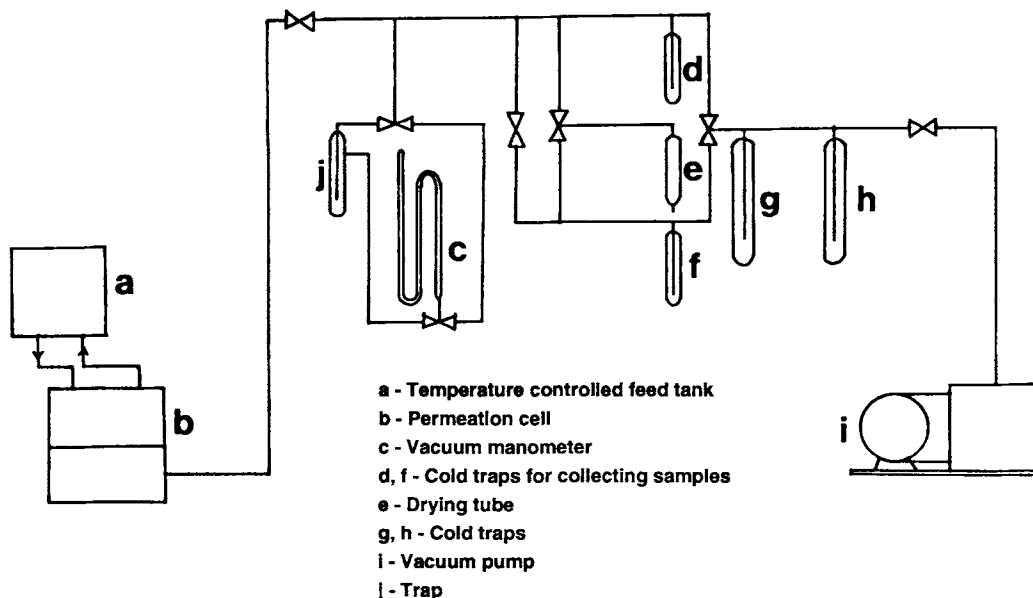g, h - Cold traps
i - Vacuum pump
j - Trap

Figure 2   Schematic diagram of pervaporation apparatus used in this study.

feed tank had a solution capacity of approximately 1000 mL. From the feed tank, which was kept at a constant temperature by the water bath, the feed mixture was circulated through the cell. The pressure at the downstream side was kept below 4 mm Hg by vacuum pump. Pervaporation experiments were conducted at 60, 70, and 75°C for ethanol–water mixtures. Upon reaching steady-state flow conditions, product samples were collected with timed intervals, isolated from the vacuum system, and weighed.

The composition analysis of the permeate was done using gas chromatography. A calibration curve of the ethanol–water mixture was prepared using known quantities of the two compounds. The following relationship was used to calculate the separation factor:

$$\alpha_{i/j} = \frac{(y_i/y_j)}{(x_i/x_j)}$$

where x is the feed composition, y is the permeate composition, and component i is the preferentially permeating component.

RESULTS AND DISCUSSION

Generally speaking, as the crosslinking density in a polymer increases, the resulting material has a more compact network structure, resulting in less chain mobility. Therefore, the free volume in the polymer

is decreased and the amount of solvent swelling as well.[10] This principle can be applied to the separation process of crosslinked polymer membranes: as the crosslinking density in the membrane increases, the solubility of the liquid mixture declines and the diffusivity, which is governed by the free volume, decreases due to the rigidity of the polymer chains. This might cause the permeation rate through the membrane to decrease. And, from the viewpoint of the separation factor, PVA is a well-known water-soluble polymer, in other words, highly hydrophilic material. This means that the hydroxyl group in PVA causes the strong hydrogen bonding with the feed mixtures (water and ethanol in this study) to be separated. In general, this hydrogen bonding force between water and PVA is stronger than that between ethanol and PVA since the PVA material shows preferential water permeation rather than ethanol permeation. However, in the case of PAA used as the crosslinking agent in this study, the carboxylic group also causes hydrogen bonding between the polymer and the individual component in the feed mixtures, i.e., water or ethanol. According to the investigation of Yoshikawa et al.,[11] the hydrogen bonding ability toward carboxylic acid decreased in the following order: water > ethanol. This means that the carboxylic group in the membrane may interact with water more preferentially than ethanol. As a result, water could be selectively absorbed and permeated into the membrane compared with ethanol. And another advantage of PAA material as the crosslinking agent is that the carboxylic group
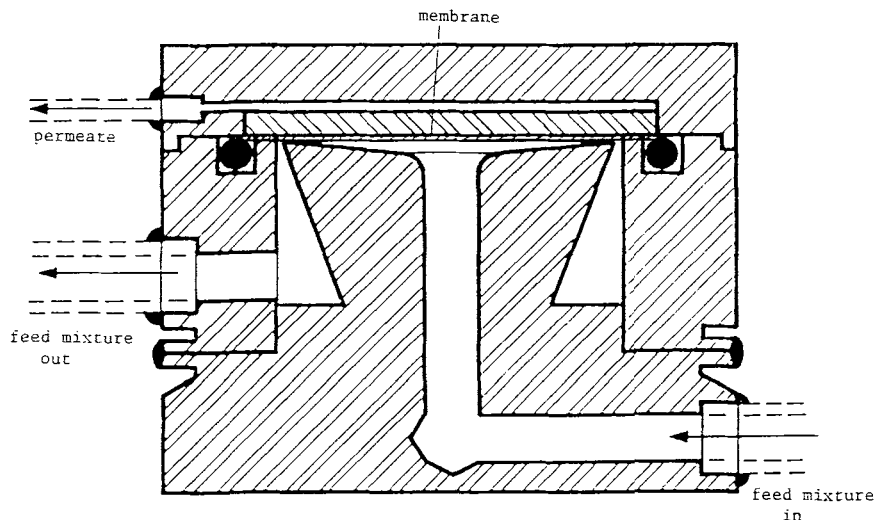
Figure 3 Configuration of the permeation cell used in this study.

at each repeating unit can be compared with the other crosslinking agent having the carboxylic group, such as maleic acid.[12]

First, the prepared membranes were tested for the ethanol : water = 50 : 50 solution at 60°C since this solution could be obtained from the separated solution from the fermentation broth with the organic selective membranes, such as poly(dimethylsiloxane) (PDMS), where the ethanol composition in the fermentation broth might be 5 to 8%. Figure 4 shows the permeation rate and separation factor for ethanol : water = 50 : 50 solution at 60°C with various PVA/PAA membranes. As expected, the permeation rate decreases with increasing crosslinking density, while the separation factor increases up to 260 for the PVA/PAA = 80/20 membrane. These data are good enough when compared

with the data from other membranes, such as cellulose acetate, cellophane, and polyetherurea.[1,2]

Therefore, we have tested several compositions of ethanol–water mixtures with various crosslinking densities of PVA/PAA blended membranes at 60, 70, and 75°C. Figures 5 and 6 illustrate the permeation rates and separation factors for ethanol : water = 80 : 20 solution by using the three kinds of blended and crosslinked membranes, respectively. As can be seen, the permeation rates increase with increasing operating temperatures, and decrease with an increasing PAA content in the resulting membranes. Lowering the operating temperature causes a stronger hydrogen bonding interaction between the membrane and each component in the feed mixture. As a result, the flux decreases and the selectivity
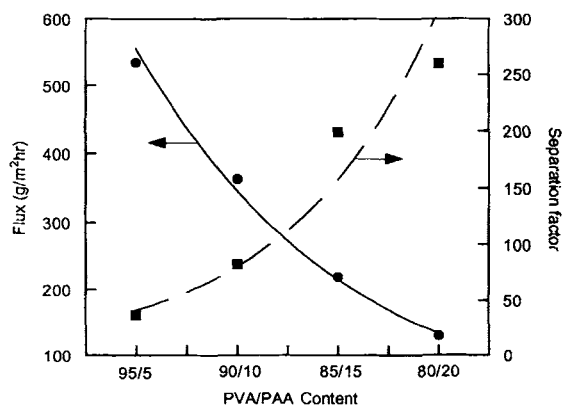

Figure 4 Permeation rate and separation factor for ethanol : water = 50 : 50 mixtures with varying PAA contents at 60°C.
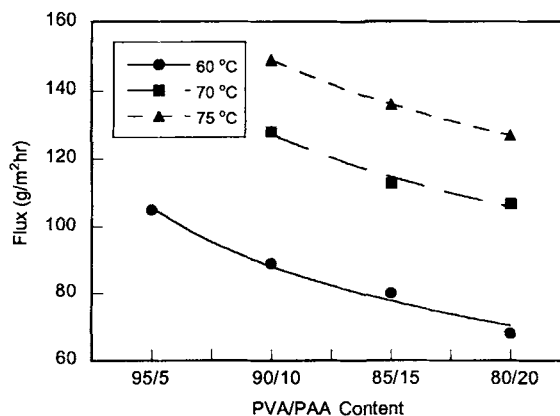

Figure 5 Permeation rates for ethanol : water = 80 : 20 mixtures with varying PAA contents at 60, 70, and 75°C.
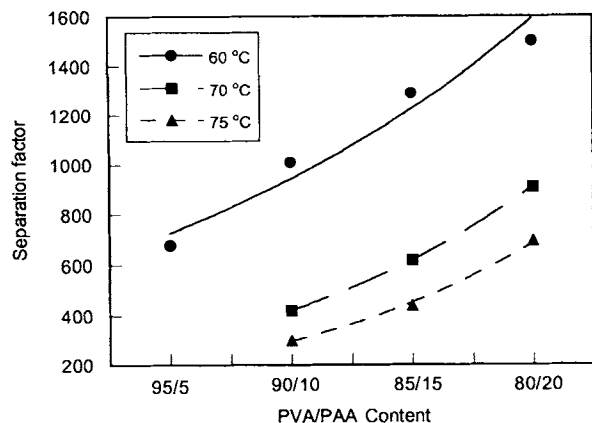
Figure 6 Separation factors for ethanol : water = 80 : 20 mixtures with varying PAA contents at 60, 70, and 75°C.

Figure 8 Separation factors for ethanol : water = 90 : 10 mixtures with varying PAA contents at 60, 70, and 75°C.

toward water increases. In addition, the separation factor increases almost up to 700 when using the PVA/PAA = 80/20 membranes at 75°C.

Figures 7 and 8 show the separation results at which the ethanol compositions in the mixtures are 90 wt %. As illustrated in Figures 7 and 8, the permeation rates are smaller than those at ethanol : water = 80 : 20, as expected, while the separation factors increase. This phenomena is very general in the pervaporation field, that is, the smaller the water portion in the mixtures, the larger the separation factor values are, and the smaller the permeation rates are. The separation factor increases to 2800, which may satisfy the required membrane performance from the viewpoint of the separation factor.[13]

The separation results at the azeotropic point of ethanol : water = 95.6 : 4.4 are shown in Figures
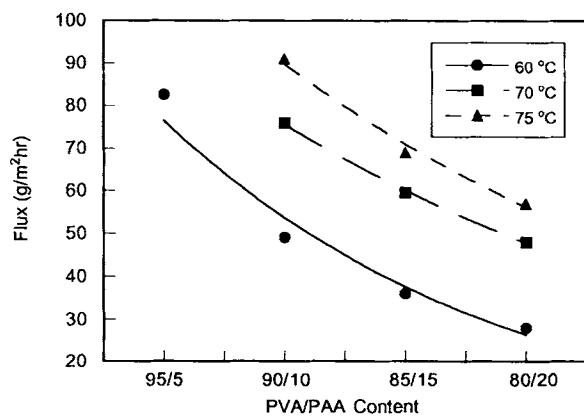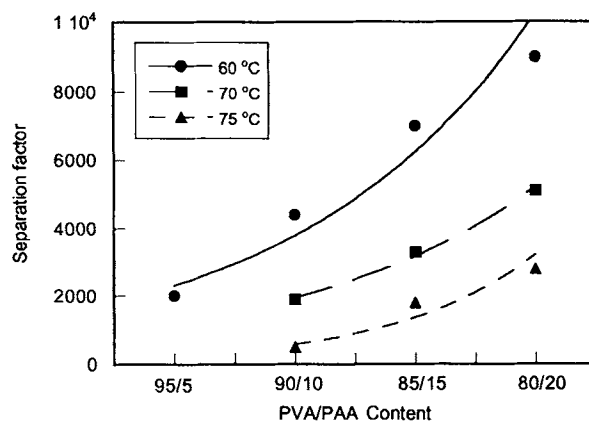
9 and 10. In this case, the permeation rate and the separation factor at 75°C are ca. 30 g/m^2/h and 5800, respectively. According to the published results of GFT membrane at this composition, the permeation rate and separation factor show 0.12 kg/m^2/h and 500, respectively.[13] Therefore, if we consider that the permeation rate will increase and the separation factor decrease in the case where the composite membrane is prepared instead of the present dense membrane; the present membrane is highly competitive with the commercial GFT membrane.

CONCLUSION

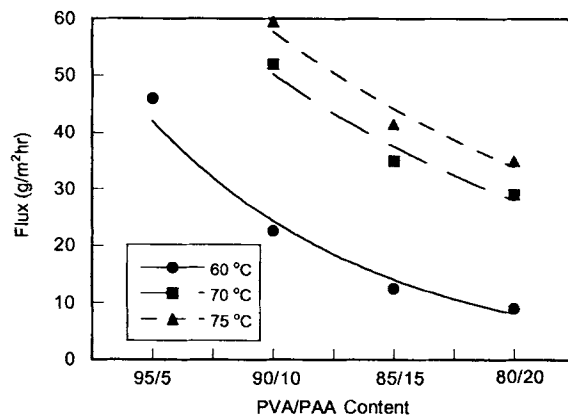The second stage process in a two-stage pervaporation process which consists of organic-selective

Figure 7 Permeation rates for ethanol : water = 90 : 10 mixtures with varying PAA contents at 60, 70, and 75°C.

Figure 9 Permeation rates for ethanol : water = 95.6 : 4.4 mixtures with varying PAA contents at 60, 70, and 75°C.
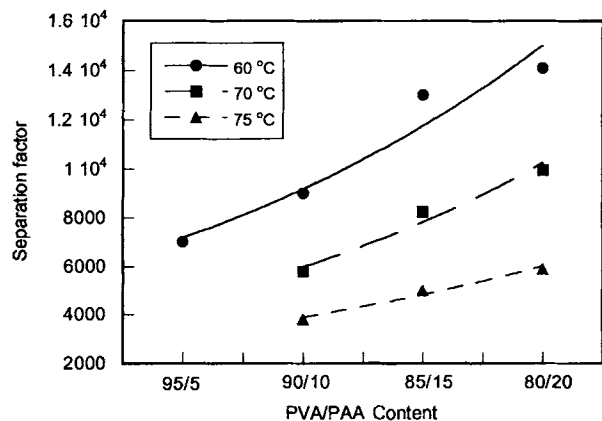
Figure 10 Separation factors for ethanol : water = 95.6 : 4.4 mixtures with varying PAA contents at 60, 70, and 75°C.

(first stage) and water-selective (second stage) process was investigated for various compositions of ethanol–water mixtures in detail using crosslinked PVA membranes with low-molecular-weight PAA as the crosslinking agent. The separation factor $\alpha_{w/e}$ = 260 was obtained for ethanol/water = 50/50 solutions at 60°C by using a PVA/PAA = 80/20 membrane. And for the ethanol/water = 90/10 solution, the PVA/PAA = 80/20 membrane showed a permeation rate 60 g/m^2/h and the separation factor $\alpha_{w/e}$ = 2800 at 75°C. The permeation rate and the separation factor at the azeotrope point of the water–ethanol mixture were 30 g/m^2/h and 5800 at 75°C, respectively, when a PVA/PAA = 80/20 membrane was used.

REFERENCES

1. I. Frennesson, G. Tragardh, and B. Hahn-Hagerdal, *Chem. Eng. Commun.*, **45**, 277–289 (1986).
2. R. Y. M. Huang and Ji-Won Rhim, *Polym. Intern.*, **30**, 123 (1993).
3. T. Q. Nguyen, A. Essamri, R. Clement, and J. Neel, *Makromol. Chem.*, **188**, 1973 (1987).
4. T. Q. Nguyen, in *Synthetic Polymeric Membranes*, B. Sedlacek and J. Kahovec, Eds., Walter de Gruyter, New York, 1987, pp. 479–494.
5. T. Q. Nguyen, A. Maazouz, and J. Neel, in *Synthetic Polymeric Membranes*, B. Sedlacek and J. Kahovec, Eds., Walter de Gruyter, New York, 1987, pp. 495–505.
6. Ji-Won Rhim, Min-Young Sohn, Hyeok-Jong Joo, and Kew-Ho Lee, *J. Appl. Polym. Sci.*, **50**, 679 (1993).
7. Ji-Won Rhim, Min-Young Sohn, and Kew-Ho Lee, *J. Appl. Polym. Sci.*, **52**, 1217 (1994).
8. M. H. V. Mulder, J. O. Hendrikman, H. Hegeman, and C. A. Smolders, *J. Membrane Sci.*, **16**, 269 (1983).
9. W. Gudernatsch, H. Strathmann, and H. Chmiel, 1st North American Membrane Society (NAMS) meeting, Cincinnati, OH, June 3–5, 1987.
10. R. Y. M. Huang and C. K. Yeom, *J. Membrane Sci.*, **51**(3), 273 (1990).
11. M. Yoshikawa, T. Yukoshi, K. Sanui, and N. Ogata, *J. Appl. Polym. Sci.: Part A: Polym. Chem.*, **24**, 1585–1597 (1986).
12. H. E. A. Bruschke, German Pat. DE3220570 A1 (1983).
13. Y. Maeda and M. Kai, in *Pervaporation Membrane Separation Processes*, R. Y. M. Huang, Ed., Elsevier Science Publishers B.V., The Netherlands, Amsterdam, 1991, Chap. 9.